

MOLECULAR SIZE LIMITS FOR ROTATIONAL SPECTROSCOPY AND THE HIGH-J LIMIT OF THE RIGID ROTOR

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Molecular rotational spectroscopy is well suited for the analysis of regioisomers, which has applications in pharmaceutical synthesis. Rotational spectroscopy offers important advantages over other chemical analysis techniques resulting from extreme sensitivity to molecular mass distribution, high accuracy molecular structure (and, therefore, rotational constant) predictions from quantum calculations, and the combination of high-spectral resolution and dynamic range. The sensitivity and range of the technique allow low abundance regioisomer impurities to be quantitatively measured without chemical separation. The challenge for rotational spectroscopy is that actual measurement challenges in pharmaceutical chemistry involve molecules in the 200-500 Da mass range. Unique features of the rotational kinetic energy levels lead to decreasing peak transition strength as the molecular size increases as well as a decrease in the frequency where the strongest transitions occur. However, special features of the high-J limit (semiclassical limit) of the rigid rotor Hamiltonian potentially mitigate these experimental difficulties and suggest that rotational spectroscopy can be applied to much larger molecules than previously expected. The rotational spectra of a series of high vapor pressure large molecules in both the limiting prolate and oblate limits are analyzed. For the prospect of analyzing larger molecules, the prolate limit appears to offer major advantages. However, experiments using pulsed-jet sources show rapid relaxation of these high-energy rotational levels and, at present, appear to reduce the major advantages suggested by the rotational spectroscopy in the high-J limit.